

SHEWADE

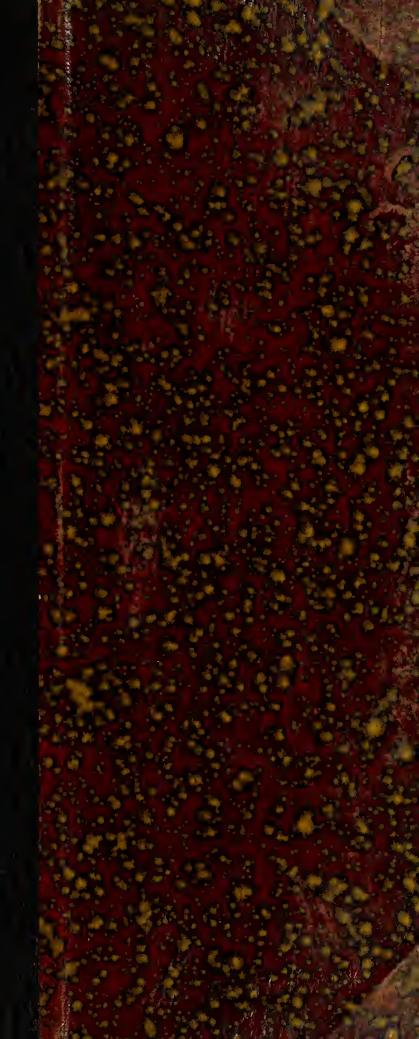
Action of Sodium on

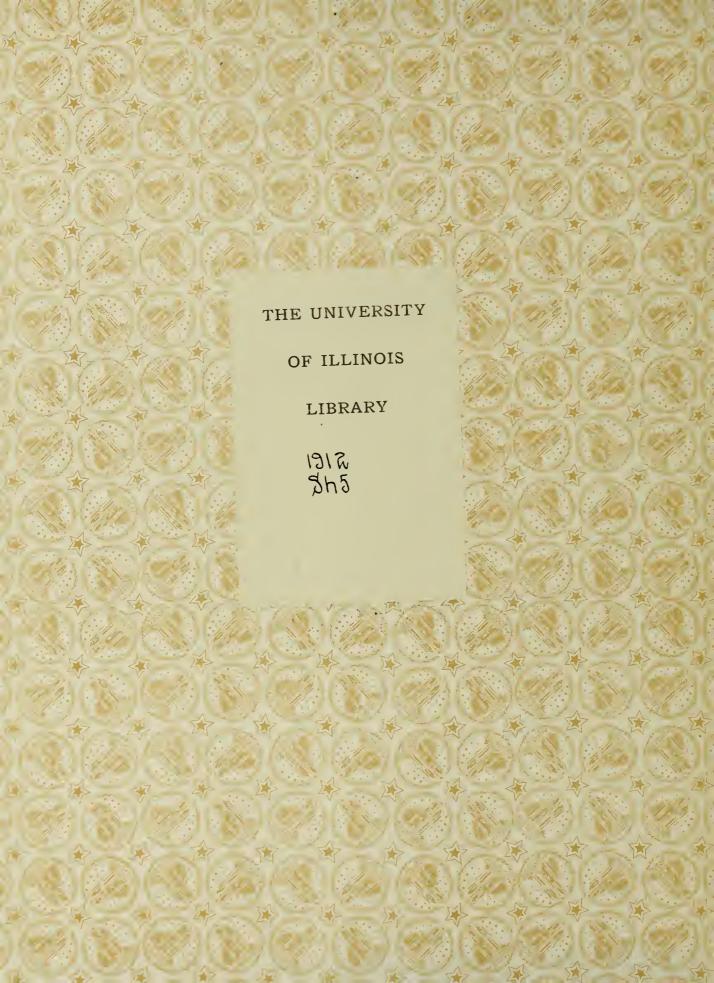
Tartronic Ester Derivatives

Chemical Engineering

B. S.

1912









ACTION OF SODIUM ON TARTRONIC ESTER DERIVATIVES

BY

VINAYAK YESHAWANT SHEWADE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1912

. 11 8 8 V

•

-)

UNIVERSITY OF ILLINOIS

MAY 3 1 1912

101

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Vinayak Yeshawant Shewade

ENTITLED The Action of Sodium on Tartronic

Ester Derivatives

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BS, in Chemical Engineering

Instructor in Charge

APPROVED: Duffarr

acting HEAD OF DEPARTMENT OF Chemic my



THE ACTION OF SODIUM ON TARTRONIC ESTER DERIVATIVES.

TABLE OF CONTENTS.

						, ,	V 41 A 4441 A			Page
I.	Int	roduo	etion							1
II. Experimental									5	
	l.	The	action	of	sodium	on	orthot	colu	idino-	
	tartronate									5
	2.	The	action	of	sodium	eth	nylate	on	orthoto-	
	luidinotartronate									6
	3.	The	action	of	sodium	on	orthot	tolu	uidino-	
		1	tartrona	te	in the	pre	sence	of	ethyliodid	le 7
	4.	The	action	of	phenyl	lıyö	lraizin	n or	ethyloxo-	- '
		r	malonate	€						7
	5.	The	action	of	phenyll	nydr	azine	on	ethyl	
dihydroxymalonate										9

Digitized by the Internet Archive in 2013

INTRODUCTION

It is a fundamental fact in organic chemistry that the hydroxyl hydrogen of alcohols is easily replaced by sodium, potassium or other metals and compounds known as alcoholates result.

Adolph Bernhard obtained sodium benzoylaceticester by the etherial solution of benzoyl aceticester with sodium, which he showed to be identical with that obtained by Claisen and Lowman², who prepared from benzoic ester, sodium ethylate, and acetic acid.

$$c_{6}H_{5}$$
 c $o = c_{1}c_{2}c_{2}H_{5}$ or $c_{6}H_{5}$ -co.chna. $c_{2}c_{2}H_{5}$

George H. U. Harrow dissolved sodium in absolute alcohol to which he added the same volume of dry ether, then solid sodium ethylate in excess, and acetic ether dissolved in an equal volume of dry ether; after evaporating the ether, sodium acetoaceticester crystallized out.

Sodium salt of malonic ester results by the addition of sodium ethylate to malonic ester.4

¹Ann. der chemie Vol. 282, pages 153, 168.

²Berichte der deut. chem. Ges. Year 1887. pp. 2178. also XX, 651.653.

³Ann. der chemie Vol.201. pp. 143.

⁴Ann. der chem. Vol. 280. pp. 264. Vol. 258. pp. 261. Vol. 266, pp. 52.



This formation is analogous to that of acetoacetic ester.

All of these salts give free esters when treated with acetic or other similar acid.

There is a considerable difference of opinion as to whether the esters have enol or ketone structure, but the question is yet unanswered.⁵

conard and Brückner⁶ have made sodium acettartronic ester, by treating the acettartronic ester with sodium.

We have made attempts to get sodium salt of orthotoluidinotartronate, by treating the tartronate with sodium, and also with sodium ethylate; but some complicated reactions take place and so far, we have not been able to separate it.

The object of the above attempts was to obtain the syrupy, uncrystallized, unstable, intermediate addition products 7 on Kete ester group $0 = \overset{\text{COOR}}{\overset{C}}{\overset{COOR}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}{\overset{C}}$

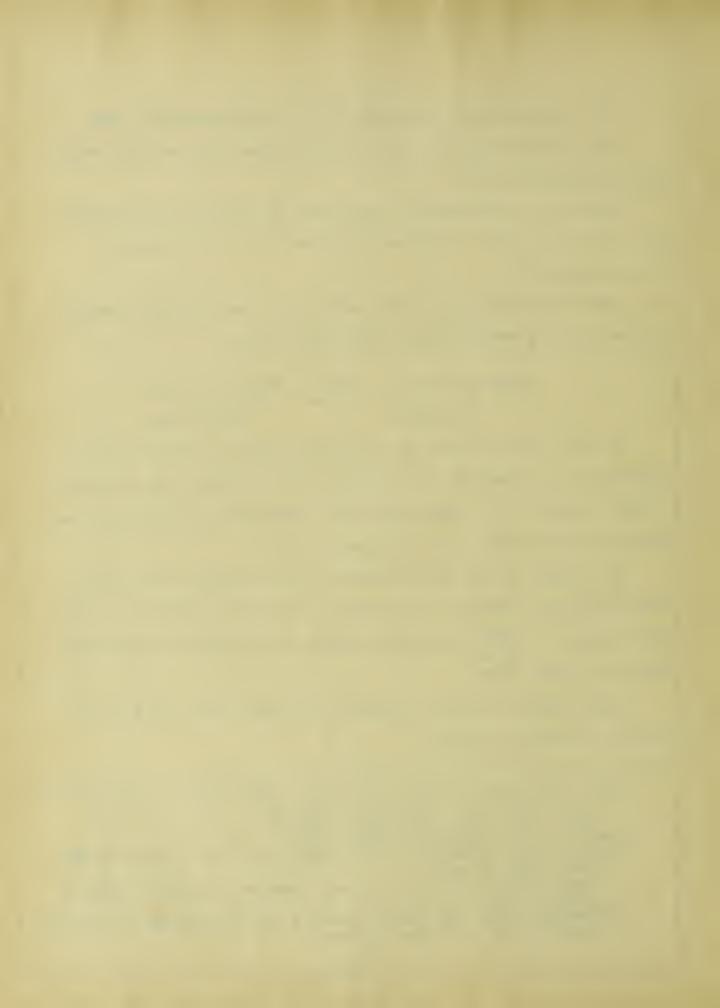
Also without trying to isolate the sodium salt, we tried to get the following reaction:

Curtiss and Stracham: - Journal American Chemical Society, XXXIII, 396.

⁵Ann. der chem. Vol. 277, pp. 162. Vol. 186, pp. 161, 214-228.
Berichte Vol. 29, 1006. Berichte XXIX, 1715. Am. chem.
jour. XVII, 437, and other papers.
6Berichte Der chem. Ges. XXIV, 2999.

⁷Curtiss and Spencer: - Journal American Chemical Society XXI. 1053; XXXIII, 985.

Curtiss, Hill and Lewis: - Journal American Chemical Society, XXXIII, 404, and other papers.



but without any satisfactory results.

Reaction of Phenyl Hydrazine on Keto ester group: -

Considering the reaction of phenylhydrazine on carbonyl group 0=C-O-R of the keto esters O=C, which is very reactive, we might O=C-O-R expect to get primary addition products

H H OH

C₆H₅-N-N-C=(COORO2, which with a removal of the elements

of water should give the corresponding hydrazones

Alfred Elber⁸ prepared phenylhydrazine-mesoxalic acid, to which he assigns the structure COOH

by the action of phenylhydrazine-hydrochloride on aqueous solution of mesoxalic acid. The substance was unstable and melted between 158° and 164° above which it decomposed completely.

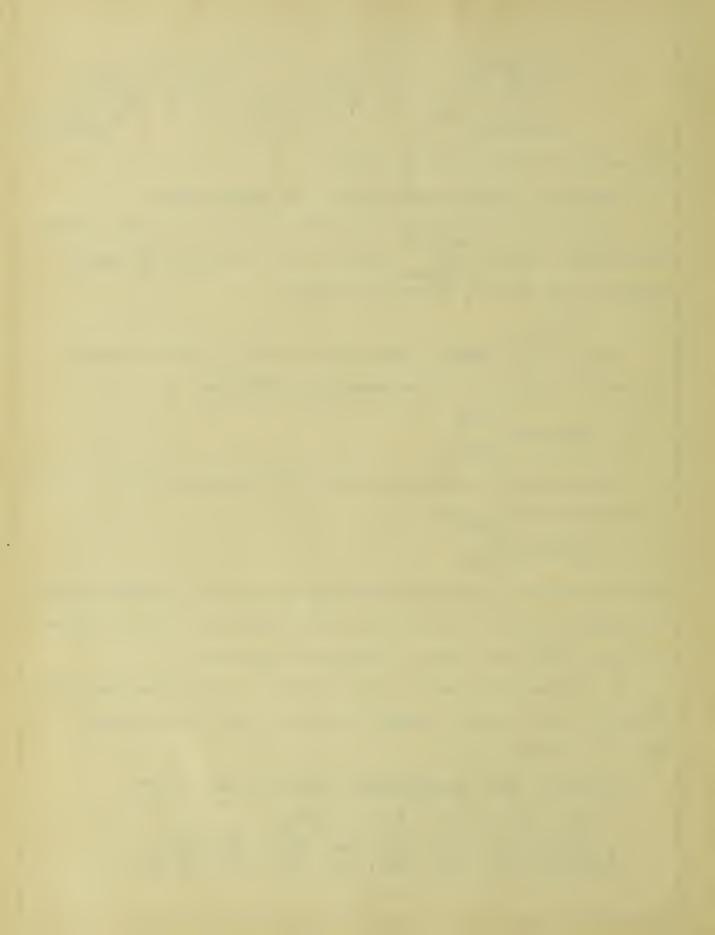
E. Fischer obtained the same product by using phenylhydrazine directly and it agreed closely in melting point and analysis to the one mentioned above.

Pechmann¹⁰ made phenylhydrozone-mesoxalicacid ester

8Ann. der chem. Vol. 227. pp. 355.
Berichte der deut. chem. Ges. XVII, pp. 578.

9Berichte der deut. chem. Ges. XVII, pp. 578.

10Berichte der deut. chem. Ges. XXII, pp. 866, 867.



from isoxazol ester, by the action of nitric acid, and subsequent treatment with soda, urea, sodium acetate and then with an acetic acid solution of phenylhydrazine. He further saponified the ester and obtained phenylhydrazine-mesoxalic acid.

Richard Meyers 11 independently prepared benzolazomalonicacid,

$$O = C - OH$$
 $O = C - OH$ $C = N - NH - C_6H_5$ $O = C - OH$ $O = C - OH$

and in order to prove that this substance was identical with that obtained by Pechmann and Fischer, he made its silver salt, and then changed it to

C. K. Hewes¹² has obtained several phenylhydrazine and substituted phenylhydrazine addition products with the methyl ester,

and also some of the corresponding hydrozones.

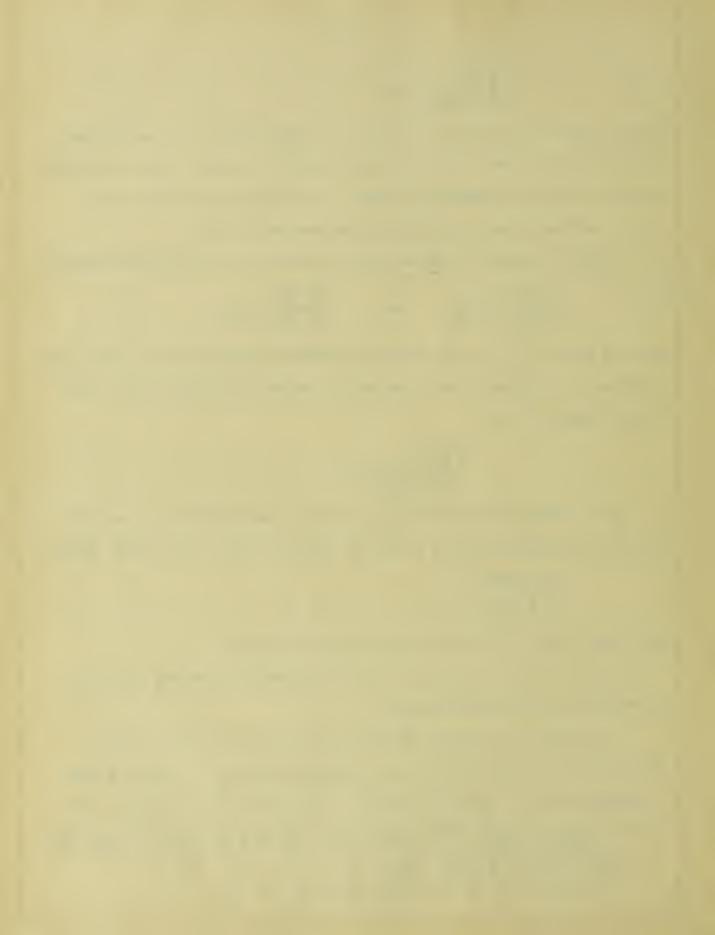
We have also succeeded in getting phenylhydrazine addition product with ethyloxomalonate.

In analogy to Fischer's work we might also obtain ethyl phenylhydrazinotartronate from phenylhydrazine and ethyl dihydroxymalonate, by partial removal of the elements of water. Our

llBerichte XXV, 3175; XXI, 118; Berichte der deut. chem. Ges XXIV, 1241-43.

^{12&}lt;sub>U</sub>. of Ill. Thesis, 1912.

¹³Berichte der deut. chem. Ges. XVII, 578.



experiments show this tendency fairly well, but the product is not analyzed due to lack of time.

EXPERIMENTAL PART

Action of Sodium on Orthotoluidinotartronate: -

Vol.1, Orthotoluidino tartronate for this purpose was pp. 85,125 and others obtained by the method of Curtiss and Hill, 14 by mixing molecular quantities of ethyloxomalonate and orthotoludine in an etherial solution.

For the reaction, 0.41 gr. of sodium was taken on one of the ends of a glass rod, which was made like a pestle, and dipped in the solution of 0.5 gr. of orthotoluidinotartronate made previously by dissolving the substance in a quantity of absolute ether just enough to dissolve the substance at ordinary room temperature. The flask was stoppered at once to shut off the moisture in the air, leaving a capillary opening at the side of the stopper to allow the evolving gas to escape. The action went very slowly, taking about twenty hours to complete the reaction. A small amount of crystalline precipitate separated, which, when looked at thru a lens appeared colorless, but its general appearance was yellow. The liquid when evaporated on a watch glass gave fine white needles, which grouped themselves in a fashion of a colony of bacteria.

The liquid itself had a strong isonitrle smell, and when evaporated resulted in a resinous mass with a few crystals in it, which became moist at about 70° and melted to a thick liquid at

¹⁴ Jour. Am. Chem. Soc. XXXIII, 404.



about 83°, returning to its original condition after cooling. The mass was crystallized from absolute alcohol and a melting point of 78°-85° was observed. This was extremely difficult to recrystallize, since the amount of crystals obtained was very small.

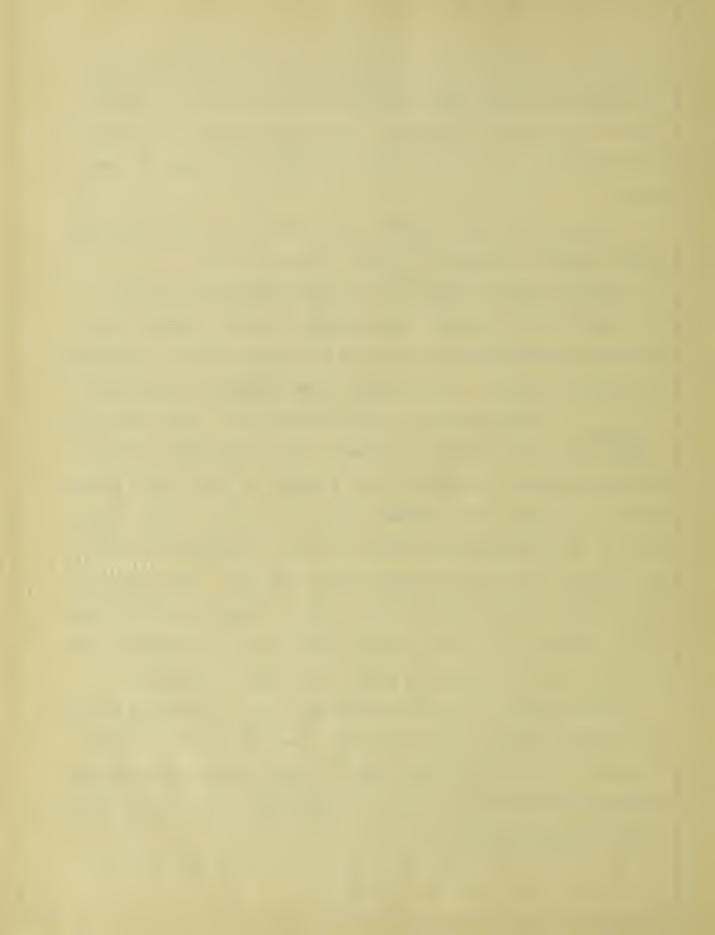
The experiment was repeated but without getting sufficient product for purification of further investigation.

Action of sodium ethylate on Orthotoluidinotartronate.

Solutions of molecular quantities of sodium ethylate and orthotoluidinotartronate were made by dissolving each separately in absolute alcohol. Upon mixing these together no change in

Volume 1, Page 111. teen minutes, crystals looking like those of the tartronate began to settle at the bottom. A little more alcohol seemed to dissolve the crystals again but not to a very large extent. The mixture which was not clear, was chilled to -18° and filtered, when more crystals were obtained. The crystals were washed and burnt on a platinum foil. Charring and residue left, showed it to be the metallic salt, but the substance was not pure and the impurities might have given the residue.

The filtrate was further evaporated down and chilled to -16° but no more crystals were obtained. The solution was further evaporated down under vacuum but no change was noticed until the evaporation was carried almost to completion, when sodium ethylate seemed to separate out.

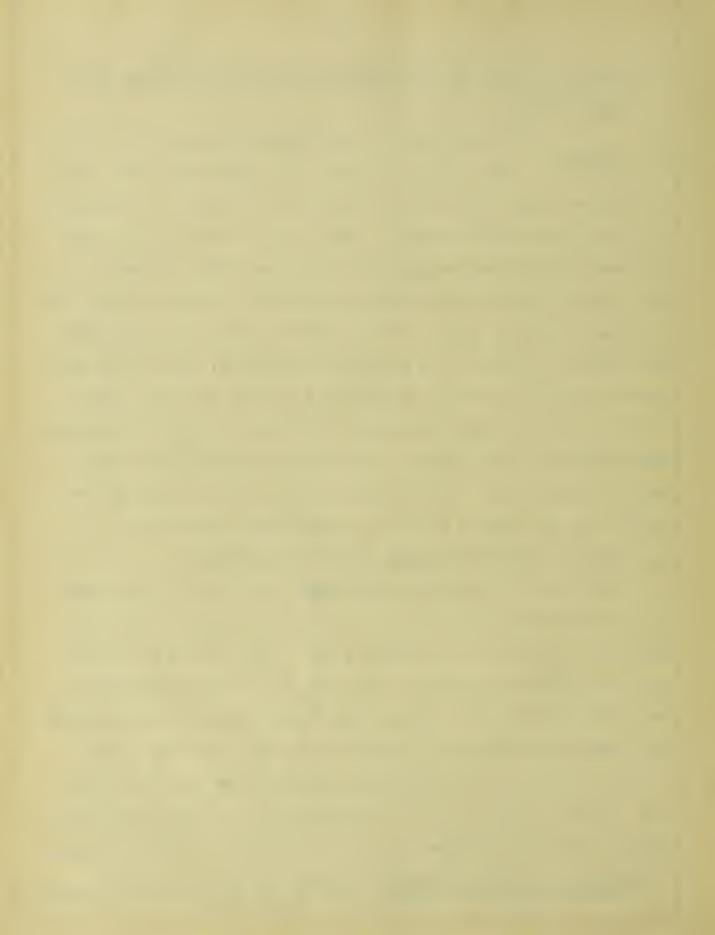


Action of sodium on Orthotoluidinotartronate in/Presence of Ethyl-Iodide.

To two grams of orthotoluidinotartronate (1 mol.) is Volume 1. pp.91,177 added 0.58 c.c.(1 mol.) of ethyliodide and 10 c.c. of absolute ether, into which 0.164 grams of sodium is introduced as in the previous experiment. After twenty-four hours all sodium was dissolved and a greenish white precipitate settled at the bottom, which did not melt even at 2400. The dark liquid had a strong isonitrile smell and the crystallization on evaporating was similar to that in the previous experiments. The liquid was further boiled in vertical condenser for about an hour. Ether and the excess of ethyliodide were distilled off, and the solution was evaporated for crystals, which, when recrystallized from absolute alcohol gave a melting point of 900, but the general behavior was the same as that of orthotoluidino tartronate.

Action of Phenylhydrazine on Ethyl Oxomalonate: -

0.985 c.c. of phenylhydrazine 108gr. i.e. 1 mol) was placed in an Erlenmeyer flask having the bottom two inches in diameter, and added 2.535 c.c. of absolute ether. The mixture was cooled to -15° in/freezing mixture, and 1.74 gr. of ethyl oxomalonate was added drop by drop, keeping the flask in the freezing mixture and thoroughly mixing the contents after each addition. With about ten minutes of stirring and vigorous rubbing with a glass rod, crystallization set in very rapidly as the ether evaporated, and in about five minutes all of it crystallized in white crystals with a trace of yellow impurity in some places. *** Vol.II.pp 38,58, and 65. Vol.III.pp 1,13,18,22,24,38,40-8-9



The crystals, which have the consistancy of paraffine, were further washed with a chilled mixture of one part benzene and five parts legroin. The yield obtained was about 50% of the keto ester used, and can be raised with a careful manipulation.

It was recrystallized from a mixture of one part of benzene and fifteen parts of legroin and analyzed.

- 1. 0.1819 gr. gave 0.3686 gr. of carbon dioxide and 0.0772 grams of water.
- 2. 0.2000 gr. gave 0.4053 gr. of carbon dioxide and 0.1021 grams of water.
- 3. 0.1748 gr. gave 0.0176 gr. of nitrogen. (16 c.c. at 742.23 mm and 24.50) over forty per cent potassium hydroxide.

Calculated for C6H5.NH.NH(OH)C (COOCH)2502

Carbon 55.32. Hydrogen 6.4. Nitrogen 9.93..percent.

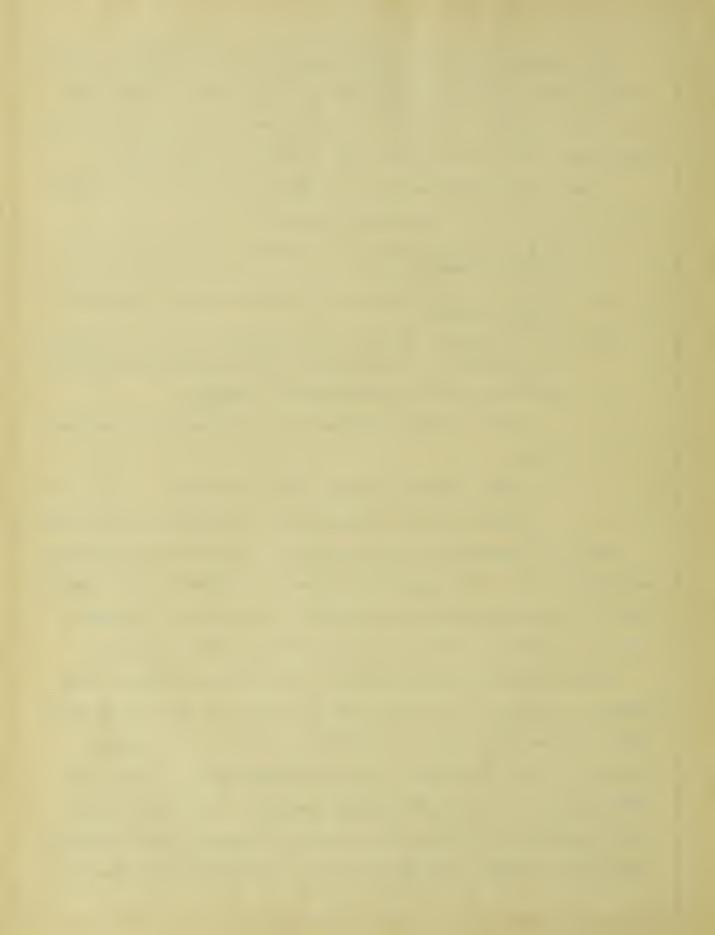
Found

Carbon 55.26. Hydrogen 4.73. Nigrogen per cent.

Carbon 55.25. Hydrogen 5.72. Nitrogen 10.06 per cent.

When the experiment is not carried at the low temperature as mentioned above, the temperature rises to 74° due to the reaction, and even the some product is obtained, the most of it seems to lose the elements of water and the yield is extremely poor.

Ethyl phenylhydrazinotartronate crystallizes from one part benzene, or ether, and fifteen parts legroin in fine white prismatic needles which melt at 53°-54° (uncorr.). It is easily soluble in ether, benzene, carbondisulphide ethyl, methyl and amyl alcohols, carbonterachloride, acetone, chloroform, xylene and ethylacetate, difficultly soluble in legroin, and apparently insoluble in water. A 10% solution of potassium hydroxide dis-



solves it to a greenish oil which floats, however, stronger solution gives a yellow solution only on heating, which after boiling and exposure to air becomes red and changes to a greenish yellow when acidified with acetic acid. On making alkaline the red color is again restored.

The color change is to be further studied.

The product is very unstable even at low temperature and time seems to be the first controlling factor. It can be kept without decomposing for two or three days only when it is in an absolutely pure condition, and kept dry and cold, about ten degrees below ordinary room temperature being enough; otherwise decomposition ensues.

The corresponding hydrozone is not crystalline and cannot be distilled.

Action of Phenylhydrazine on Ethyl Dihydroxymalonate.

Mixed 3.84 grams of ethyl dihydroxymalonate (1 mol)

Volume III. and 2.16 grams of phenylhydrazine (1 mol) Page 41. together. The dihydroxy crystals dissolved slowly resulting in an aqueous emulsion. After chilling and introducing some of the crystals from the oxomalonate addition product, the mixture crystallized rapidly. The crystals were filtered and washed as in the previous experiment; but in order to get the product in pure form, they have to be recrystallized two or three times, since the product is not so pure as in the other case.

The product is not analyzed due to lack of time, but the solubility, melting point, and stability show it to be the same as one obtained from phenylhydrazine and ethyloxomalonate.

Study of this reaction is to be continued.





